

Sulfur – a new information on this seemingly well-known element

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Abstract

Melting of orthorhombic sulfur (α -S) was investigated using DSC and X-ray analysis. It was found that reversible transformation orthorhombic to triclinic modification precedes melting. DSC and Raman spectroscopy study indicate that so-called λ -transition is reversible one and opening of S_8 rings and S_n formation seems not to be a predominant process at that transition. Viscosity glass transition of glassy sulfur prepared by rapid cooling of equilibrium melt in the temperature region of anomalous viscosity doesn't depend on melt temperature, but temperature dependence of undercooled melt viscosity (so-called fragility) does. When equilibrium temperature increases, undercooled melt becomes stronger, according to Angell's classification.

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1. Introduction

The study of elemental sulfur could seem to be a little bit surprising, because the history of this element is very old. Homer had already mentioned this element in connection with use of burning sulfur like disinfectant. Rapid development in the field of material research and substitution of oxygen with chalcogens in the new materials for optics and semiconductor technology focused the attention on sulfur again [1-3]. Specially, in the case of non-stoichiometric compounds with high overstoichiometry of sulfur there is a problem with their hardly reproducible preparation and thus changing physicochemical properties. Detailed study of elemental sulfur with help of new and more sensitive techniques shows that this element has been making the challenge for basic research [4,5]. Sulfur is an element attracting the attention because of variety of allotropic forms in the solid. The stable modification at room temperature is orthorhombic sulfur (α -S); its structure is constituted by packing of crown-like S_8 rings (*cycloocta-sulfur*). This modification converts into monoclinic one (β -S) at ~ 95 °C, melting at 115 °C. It was found that liquid sulfur with low viscosity consists mainly of S_8 -rings. With increasing temperature at ~ 159 °C small endothermic change, known as λ -transition, appears and above this temperature sulfur viscosity increases steeply. λ -transition has been mostly explained as opening of S_8 rings and their subsequent polymerization into long S_n -chains. Another possible explanation rarely used is that the λ -transition can be understood as a gelation transition [6]. But it must be pointed out, despite a large amount of experimental and theoretical investigations, that no model satisfactorily describing λ -transition is available. Properties of sulfur melt bear on the glass transition temperature being stated in wide temperature range approx. -40 to -20 °C. It depends on thermal history and on structure of melt used for glass preparation.

This work is aimed on melting of sulfur crystals, λ -transition and on the dependence of glass transition temperature on the temperature of equilibrium melt from which glassy sulfur was prepared.

2. Experimental

The pure orthorhombic sulfur modification (α -S) was prepared by crystallization of carbon disulfide sulfur solution. Purity and crystal modification was confirmed by XRD KappaCCD (Bruker), MoK_{α} , $\lambda = 7.1073$ nm, 150 K. The same diffractometer was used for the study of crystal melting, too. The temperature dependent Raman spectra were taken with triple monochromator T 64000 (JobinYvon) in back-scattering configuration using Kr^+ laser (647.1 nm excitation line), laser power 3 mW at a sample and spectral resolution of 1 cm^{-1} . Thermoanalytical properties of sulfur were studied by DSC Pyris I (Perkin-Elmer). Conventional DSC as well as StepScan DSC was used. Glassy sulfur was prepared directly in calorimeter by melt cooling from different temperatures below and above λ -transition

and also above viscosity maximum temperature (140 - 220 °C). Melt was cooled down to -65 °C with maximal achievable cooling rate. Glass transition temperature was then measured with heating rate 10 K/min.

3. Results and Discussion

One can find everywhere that, when heated over 95.3 °C, orthorhombic sulfur turns to monoclinic form (β -S). This β -S subsequently melts in temperature interval approx. 115 - 121 °C. However, our DSC measurement shows that pure α -S exhibits almost insignificant endothermic change at temperature close above ~ 100 °C followed by melting peak ($T_p = 116.5$ °C), melting enthalpy $\Delta H_m = 59.2$ J/g, see Fig. 1, curve 1. Thus pure orthorhombic sulfur does not undergo polymorph change $\alpha \rightarrow \beta$, and α -S melts at 116.5 °C. Explanation of this surprising result one can probably find only in the Remy's Inorganic Chemistry [7], who states that the polymorphs change $\alpha \rightarrow \beta$ occurs only if β phase is present at least in some trace. It was not our case, indeed, and so no transformation could be observed. Therefore we could focus our attention to the melting of α -S crystals. Temperature dependent XRD diffraction of α -S monocrystal shows surprising fact that α -S is not the crystal form which melts. We have found that at 116.0 °C, closely before melting, orthorhombic to triclinic transformation takes place (99.810°, 101.794°, 99.213°; unit cell volume 271.6 Å³). This transformation is reversible, at cooling the triclinic phase turns back to orthorhombic one (unit cell volume 3309.3 Å³). When temperature reaches 116.3 °C, the triclinic phase remains preserved but angles are changed (104.13°, 104.0°, 101.91°) and unit cell volume increases to 823 Å³. Further increase of temperature finally results in the collapse of long-range crystal structure and leads to the melting.

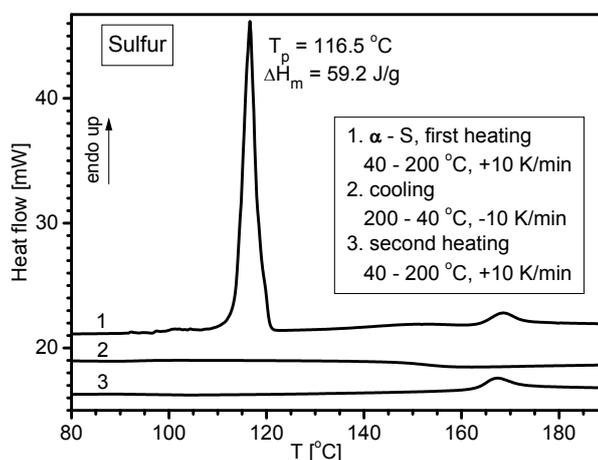


Fig. 1 Set of conventional DSC scans starting with α -sulfur. For more details, see text.

During heating of melt insignificant endothermic change of unclear origin spread out over approx. 35 °C range ($T_p = 149.5$ °C, $\Delta H = 1.9$ J/g) occurs, followed by so-called λ -transition. It is supposed that at λ -transition some of the S₈ rings break and polymer chains of sulfur are formed and this causes the sudden and very large increase in viscosity, see [9] and refs. cited in. However, taking in mind energy of S-S bond 2.2 eV the wide-spread idea of breaking of S-S covalent bonds at ~ 160 °C, only 40 °C above molecular crystal melting temperature, seems to be unrealistic.

When molten sulfur is cooled down from temperature above λ -transition, the sigmoidal change of heat flow with relatively big decrease of isobaric heat capacity can be observed by conventional DSC (inflex temperature $T_{\text{inflex}} = 153.4$ °C, $\Delta C_p = -0.35$ J/(g.K), cooling rate -10 K/min), Fig. 1, curve 2. Being measured by conventional DSC this change isn't accompanied by visible enthalpic change. However, the StepScan DSC technique shows, beside slightly different temperature of that effect, that sigmoidal transition ($T_{\text{inflex}} = 158.5$ °C, $\Delta C_p = -0.57$ J/(g.K)) corresponds well with the λ -transition ($T_{\text{inflex}} = 159.3$ °C, $\Delta C_p = +0.57$ J/(g.K)) and its exothermic change -1.15 J/g is close to the endothermic change at λ -transition (+ 1.20 J/g). At this moment, we'd like to stress that λ -transition endothermic change is extremely small for breaking covalent S-S bonds. The reason why conventional DSC and StepScan DSC results differs a little, see e.g. [8]. We have also found that even though sulfur didn't crystallize during cooling, in the subsequent heating scan λ -transition remained, only at slightly lower temperature (approx. 1.5 °C), see Fig. 1, curve 3, as well as its sigmoidal counterpart at cooling.

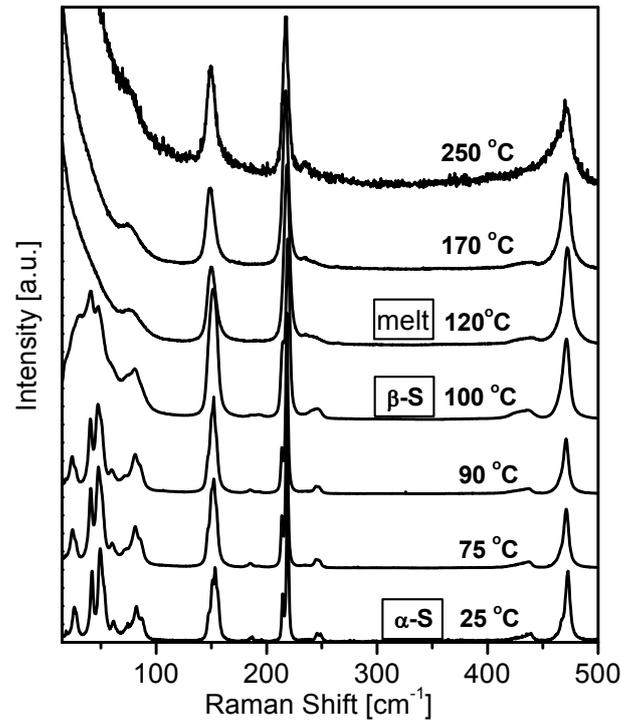


Fig. 2 Temperature dependence of Raman spectra of distilled sulfur.

Raman spectroscopy was used for monitoring of the temperature dependence of structural changes of sulfur, Fig. 2.

High purity sulfur distilled under argon atmosphere, not only pure α -S modification used in our other experiments, was used to have a possibility observing difference between spectra of orthorhombic (α -S) *cycloocta*-sulfur and monoclinic (β -S) one. Spectra can be divided into two energy regions. First of them ($100\text{--}500\text{ cm}^{-1}$) covers energy range of sulfur molecules fundamental vibrations and second region, at energies lower than 100 cm^{-1} , purveys information about lattice vibration. Our results show no significant temperature dependent changes in the energy

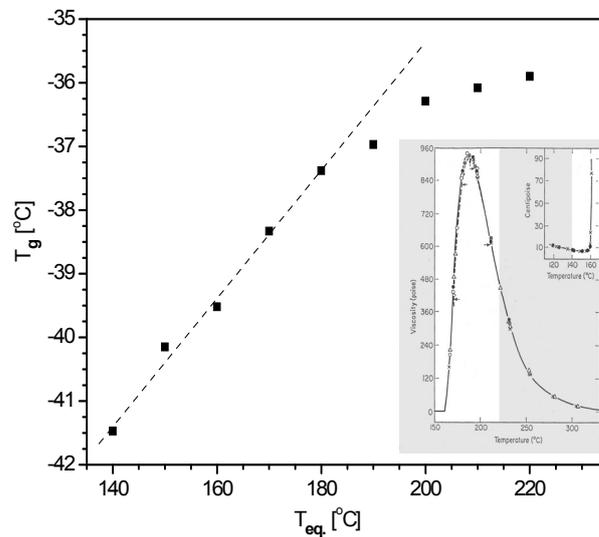


Fig. 3 Dependence of glass transition temperature on melt equilibrium temperature T_{eq} , see text. Inset: Temperature dependence of sulfur viscosity [9]. White areas cover experimental temperatures.

range of sulfur molecules vibration, so that it is clear that S_8 rings remain unchanged over the whole temperature interval ($25\text{--}250\text{ °C}$). On the contrary, significant changes of spectrum shape are evident at energies characteristic for sulfur molecules arrangement in crystalline modifications or phases. One can see that both crystalline modifications of sulfur and the sulfur melt can be clearly distinguished at low energy region, Fig. 2. The marginal influence of

temperature on vibrational spectrum of *cycloocta*-sulfur molecule shows that the opening of S_8 rings and formation of S_n chains of various lengths cannot be supposed, at least not in detectable concentrations. If sulfur chains have been formed the number of Raman active fundamental vibrations would change. Shape of sulfur molecule vibrational spectrum should be changed in this case but, as one can see in Fig. 2, the S_8 -molecules Raman spectrum keeps unchanged aside from temperature, except spectrum measured at 250 °C, where broadening of 472 cm^{-1} band is caused by the most intensive 459 cm^{-1} band of S_n (for detailed spectrum of S_n , see [9]).

To test temperature influence on properties of sulfur melt, the calorimetric glass transition temperature was monitored on the set of nine samples prepared by cooling of melts equilibrated at temperature range 140-220 °C. These temperatures start nearly 20 °C below λ -transition and cover almost the whole range of anomalous temperature dependence of sulfur viscosity, inset in Fig. 3.

Glass transition temperature (the temperature at $\Delta C_p/2$) increases linearly when equilibrium melt temperature rises up to $T_{eq} = 180$ °C, close to the viscosity maximum, and at higher temperatures glass transition temperature increases still slower and slower, Fig. 3. The isobaric heat capacity change at glass transition, $\Delta C_p = 0.19 \pm 0.01$ J/(g.K), is practically independent on melt equilibrium temperature, T_{eq} . Glass transition temperatures of glassy sulfur prepared by cooling of relatively cold and viscous melts are markedly lower than glass transition temperatures of glassy sulfur prepared from low viscous melt ($T_{eq} \sim 300$ °C) by quenching into liquid nitrogen ($T_g = -25.6$ °C, $\Delta C_p = 0.20$ J/(g.K); StepScan DSC). Glass transition obtained in this way is close to usually stated $T_g = -27$ °C, [10].

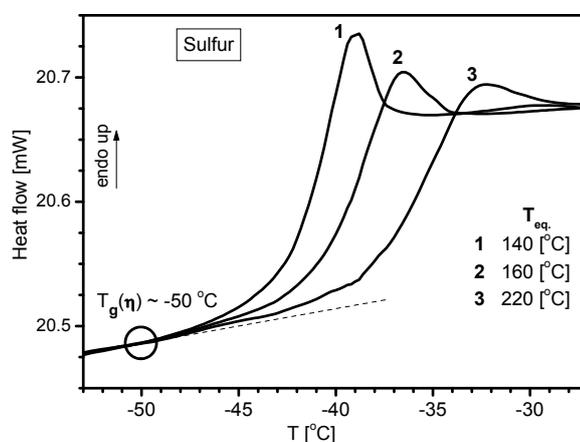


Fig. 4 Example of width of the glass transition region broadening when melt equilibrium temperature T_{eq} increases. Viscosity glass transition is also indicated.

Surprisingly, with increasing equilibrium melt temperature foregoing glass preparation, T_{eq} , temperature difference between onset and endset of transition, i.e. the width of glass transition, increases but the glass transition onset temperature remains always unchanged, see Fig. 4.

This onset temperature corresponds to the viscosity glass transition temperature, $T_g(\eta = 10^{12}$ Pa.s) [11], and the width and steepness of the glass transition are related to the melt fragility (classification is based on temperature dependence of viscosity according to Angell fragility concept [12-14]). From it follows that viscosity glass transition temperature of glassy sulfur prepared by aforesaid process doesn't depend on equilibrium melt temperature before glass preparation, however, undercooled sulfur melt (melt being out of thermodynamic equilibrium) close to the viscosity glass transition temperature is becoming more and more stronger. We suppose progressive breaking-up of crystal fragments, but still preserving crystal structure (it means decreasing fragments dimension by breaking of weak van der Waals interactions among electroneutral sulfur molecules, but without significant covalent S-S bond breaking). Consequently relative ratio of weak bonds decreases and probably as a result melt becomes stronger with increasing temperature. This point of view also agrees well with above mentioned opinion that very small enthalpic change at λ -transition isn't sufficient to be related to S-S covalent bond breaking.

4. Conclusion

DSC measurement shows that pure orthorhombic sulfur (α -S) does not undergo polymorph change $\alpha \rightarrow \beta$ and α -S melts at 116.5 °C, $\Delta H_m = 59.2$ J/g.

Detailed XRD analysis of melting process recovers that in fact α -S modification doesn't melt. Reversible transformation of orthorhombic to triclinic modification was found at 116.0 °C followed by subsequent transformation to another triclinic modification at 116.3 °C which is the one melting.

Raman spectroscopy didn't find any changes of S₈ molecule spectrum shape over wide temperature interval covering temperatures of all the most important structural and phase changes.

Both conventional DSC and StepScan DSC showed that λ -transition is reversible one accompanied by enthalpic changes close to ± 1.2 J/g, too low to be sufficient for S-S covalent bond breaking.

Calorimetric glass transition temperature and temperature width of this transition increase, and because ΔC_p remains practically unchanged, steepness of transition decreases when equilibrium melt temperature rises up before glass preparation, however, viscosity glass transition remains unchanged at the same time. From it follows that undercooled sulfur melt close to the viscosity glass transition temperature is becoming increasingly stronger when equilibrium melt temperature increases. However, viscosity glass transition remains unchanged at the same time. We suppose progressive breaking-up of crystal fragments with equilibrium melt temperature but without significant breaking of covalent S-S bonds. Relative ratio of intermolecular weak bonds decreases and, probably as a result, melt becomes stronger. Unfortunately, insensitivity of viscosity glass transition temperature (or onset of calorimetric glass transition) on temperature of equilibrated sulfur melt and thus on its structure is not clear, yet.

Bearing in the mind three experimental results: i) λ -transition is reversible, ii) Raman spectra of *cycloocta*-sulfur keep unchanged aside from temperature, except slight change of spectrum measured at 250 °C, and iii) glasses can be prepared by melt cooling from temperatures sufficiently below λ -transition, the widely spread idea of S₈ rings opening and formation of S_n chains at λ -transition should be re-examine.

Acknowledgements

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